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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for the production of Alpha, Beta Unsaturated Carbonyl Compounds

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing alpha,beta-unsaturated carbonyl compounds of increased molecular weight by the condensation of carbonyl compounds of relatively lower molecular weight. More particularly, it relates to a process wherein aldehydes or ketones or mixtures thereof are aldolized and dehydrated in the presence of a solid, insoluble catalyst comprising the reaction product of molybdenum oxide and magnesium oxide or alternatively a solid, insoluble catalyst which comprises in addition zinc oxide.

The liquid phase aldolization of aldehydes or ketones in the presence of strong bases is well known in the art. The hydroxy carbonyl or aldol compounds formed in the presence of these catalysts are generally subjected to a subsequent dehydration step in order to produce the corresponding alpha, beta-unsaturated aldehydes or ketones. Difficulties are experienced in such processes, however, because the strong bases tend to promote further reaction of the products which initially result from the simple condensation of two carbonyl molecules. Consequently, the yields of alpha,beta-unsaturated carbonyl compounds from such processes are generally unsatisfactory, and the isolation of pure products is difficult.

The production of alpha,beta-unsaturated carbonyl compounds by passing carbonyl re-

actants in the vapor phase at elevated temperatures over a fixed catalyst bed is also known. However, the yields of alpha, beta-unsaturated products are generally low per pass and, in addition, one must contend with the disadvantages inherent in vapor phase operations.

More recently, it has been discovered that alpha, beta-unsaturated carbonyl compounds are produced by heating, for example, aldehydes in the liquid phase with metal soap catalysts which are soluble therein. To a greater or lesser degree, the soaps of a wide variety of metals, for example, cobalt, manganese, magnesium, zinc and lead, have been found to be catalytically active. Generally, the conversions and selectivities to alpha, beta-unsaturated aldehydes are high in the soap-catalyzed processes; however, use of the soluble soap catalysts presents an additional problem. Before the alpha, beta-unsaturated product can be processed further, for example, by hydrogenation to the corresponding alcohols, the soluble catalyst content must be reduced to below 20 ppm. While unsuitable demetalling processes are known to the art, this additional processing step necessarily adds to the ultimate cost of the product.

These and other disadvantages of the prior art processes for producing alpha, beta-unsaturated carbonyl compounds of increased molecular weight from carbonyl compounds of relatively lower molecular weight are overcome by the present invention.

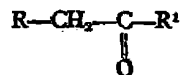
It has now been found that alpha, beta-unsaturated carbonyl compounds can readily and conveniently be produced by contacting two molecules of the same or different "monomer" aldehyde or ketone in liquid phase and at elevated temperatures with a catalyst comprising the reaction product of molybdenum oxide and magnesium oxide or

with a catalyst which comprises in addition zinc oxide. High conversions of the reactants and high selectivities to the desired alpha, beta - unsaturated carbonyl products are realised by this novel process. Furthermore, since the oxide reaction product catalyst is substantially insoluble in the reactants and in the products, its use in liquid phase aldolization processes as described herein effectively eliminates the necessity for subjecting the products to a demetalling step.

The process of the present invention is applicable to a wide variety of aldehyde, ketone, and mixed aldehyde-ketone feeds.

- 15 In order to obtain alpha, beta-unsaturated carbonyl products, it is necessary that the feed employed in the process comprise an aliphatic aldehyde or ketone having at least two alpha hydrogen atoms, i.e. at least two hydrogen atoms bonded to a carbon atom

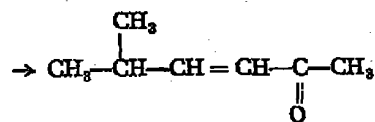
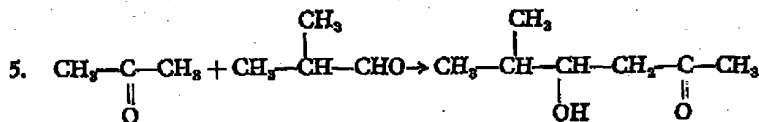
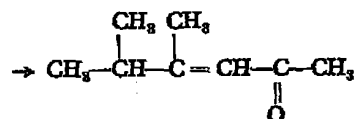
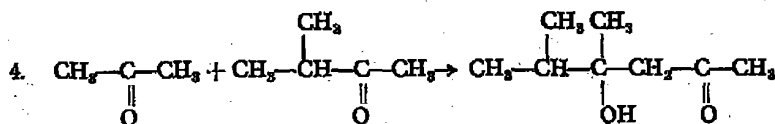
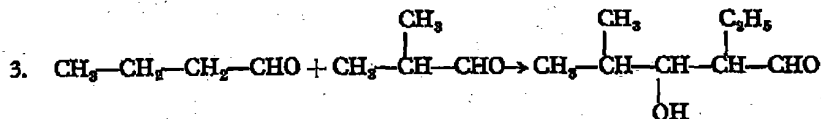
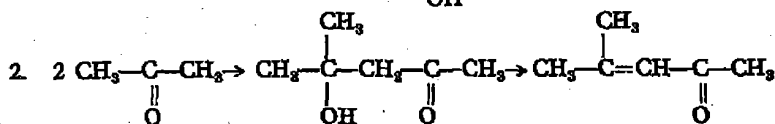
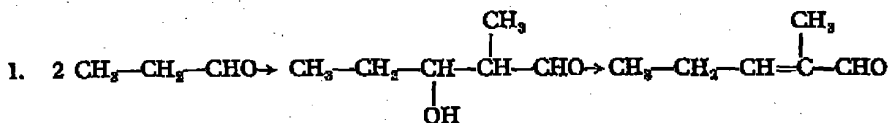
next adjacent the carbonyl group. That is to say, the feed to the process must contain at least one C₂ to C₂₀ reactant having the general formula:



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where R and R¹ can be the same or different and represent a hydrogen atom or an alkyl radical. Mixed feeds are also suitable in the present process, i.e., the feed may comprise one ketone, two different aldehydes or different ketones, or one aldehyde and one ketone. Typical combinations of reactants are shown in the following equations in which representative carbonyl compounds are used for purposes of illustration.

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While any combinations of reactants such as those illustrated may serve as the feed to the present process, it will be recognized that where more than one molecular species of reactant is employed, mixtures of products are produced. To minimize the problems associated with the separation of complex mixtures, it is preferred to select reactants or ratios thereof so that the production of a single product is favored. For example, by having only one molecular species of aldehyde or ketone in the feed, or where more than a single species is present, employing the less reactive species in excess, the production of a single alpha, beta-unsaturated carbonyl product is promoted.

Of the wide variety of reactants and combinations thereof which may be used as feeds in the present process, the aliphatic carbonyl compounds having at least two alpha hydrogen atoms are preferred, and especially, the C_2 to C_{10} aliphatic aldehydes and C_3 to C_{10} ketones, e.g. acetaldehyde, propionaldehyde, n-butyraldehyde, acetone, methyl ethyl ketone, n-octylaldehyde, n-decylaldehyde, 2-ethylhexaldehyde, methyl isobutyl ketone and methyl isoamyl ketone, and the like. Of course, an aldehyde or ketone which does not contain two alpha hydrogen atoms, e.g. formaldehyde, may be a reactant in the present process provided the reaction mixture also contains a carbonyl compound having the required alpha hydrogen atoms.

As noted hereinabove, the catalysts of the present process comprise molybdenum oxide and magnesium oxide in chemical combination. That is to say, the catalysts of this invention contain as the active ingredient a reaction product such as that obtained when a mixture of molybdenum oxide and magnesium oxide, i.e. MoO_3 and MgO , is calcined. The nature of the resultant product is not known with certainty; however, it is known to comprise the oxides in a chemically reacted form. A mere physical mixture of the oxides is not produced, for the reaction product does not exhibit the characteristic X-ray diffraction patterns of the individual oxide components. While we do not wish to be bound by any theory, it appears that at elevated temperatures the molybdenum and magnesium oxides react to form a hard, durable, amorphous, spinel-type material.

The preferred catalysts of the present process comprise molybdenum oxide, magnesium oxide and zinc oxide. That is to say, the preferred catalysts of this invention contain as the active ingredient a product such as that obtained when a mixture of molybdenum oxide, magnesium oxide and zinc oxide, i.e. MoO_3 , MgO and ZnO , is calcined. The nature of the resultant product is not known with certainty; however, it is known to comprise the oxides of molybdenum and magnesium in a chemically reacted form in com-

bination with zinc oxide. A mere physical mixture of the oxides is not produced, for the calcined product, while showing the presence of zinc oxide, does not exhibit the characteristic X-ray diffraction patterns of the molybdenum or magnesium oxides. While we do not wish to be bound by any theory, it appears that at elevated temperatures the molybdenum and magnesium oxides react to form a hard, durable, amorphous, spinel-type material within which free zinc oxide is physically entrapped.

The ratio of oxides used to produce the MoO_3 - MgO reaction product may be varied considerably. For example, from 0.5 to 15 parts by weight of molybdenum oxide per part of magnesium oxide can be used. However, the reaction product obtained upon calcining a mixture containing from 0.8 to 5 parts by weight of MoO_3 per part of MgO oxide is preferred and especially that product derived from equimolar amounts of the two oxides, i.e. 3.6 parts of MoO_3 per part of MgO . The ratio of oxides in the ZnO -containing catalyst composition may be varied considerably. For example, weight ratios of $MoO_3/MgO/ZnO$ within the ranges of 1-15/1-2/1-4 can be used. However, the product obtained upon calcining equimolar amounts of the three oxides, i.e. about 3.6 parts of MoO_3 per part of MgO per 2 parts of ZnO is preferred. It is, of course, not required that MoO_3 , MgO and ZnO themselves be used to obtain the desired reaction product. Any inorganic or organic compounds of the metals which upon calcining will form the respective oxides, e.g., nitrates, carbonates, hydroxides, acetates and oxalates may also be used. Calcining temperatures will vary somewhat depending upon the nature of the compounds employed, but in general will be from 300° to 1500° F., e.g. 1100° F.

The oxide reaction product may be utilized in various forms, for example, the product *per se* may be crushed to suitable size and packed to form a solid catalyst bed, or it may be powdered and pelletized, piled or compacted into various shapes. It may also be employed as the active ingredient in combination with a catalyst support or carrier such as alumina, bauxite, coke, kieselguhr, limestone, silica gel and similar materials well known in the catalyst art. Those materials characterized as high surface area supports, i.e. those providing surface areas in excess of 100 square meters per gram, are preferred, especially alumina. Any of the means commonly employed to produce supported oxide catalysts may be used. (See, for example, U.S. Patent 2,888,396). Generally, the supported catalyst will contain from 1 to 20 wt. %, preferably 5 to 15 wt. %, of the reaction product of the molybdenum and magnesium oxides or from 5 to 35 wt. %, preferably 5 to 15 wt. % of the tricomponent

oxide catalyst. Although compositions outside of these ranges can be used, they are effective to a lesser degree.

The process of the invention is carried out in the liquid phase at elevated temperatures. That is to say, the carbonyl reactant or reactants, either in the presence or absence of an inert solvent, e.g. aliphatic or aromatic hydrocarbons, is contacted as a liquid with the molybdenum oxide-magnesium oxide reaction product or molybdenum oxide-magnesium oxide-zinc oxide catalyst at a temperature from 50° F. to 600° F. The exact temperature to be used is not critical and is somewhat dependent on the particular carbonyl reactant or combination thereof in the feed. Whether or not a diluting solvent is employed, as well as the time of contact with the catalyst which may vary from 5 minutes to 4 hours, will also, to some extent, determine the reaction temperature. With most carbonyl reactants, and especially with the C_1 to C_{10} aliphatic carbonyl compounds, a temperature of 100° F. to 400° F., with contact times from 15 minutes to 2 hours, is preferred.

The pressure at which the process is carried out must exceed the vapor pressure of the reaction mixture at the operating temperature, that is, the pressure should be sufficient to maintain a liquid reactant phase in contact with the catalyst. Otherwise, the pressure is not critical and atmospheric, sub-atmospheric, or superatmospheric pressures may be employed. With the lower molecular weight reactants, e.g. C_1 to C_{10} aldehydes or ketones pressures slightly above atmospheric are required to maintain the reactants in the liquid phase. On the other hand, with the higher molecular weight reactants, e.g. C_{11} to C_{200} it may be desirable to use slightly reduced pressures. Where the reaction is carried out under superatmospheric pressures, the autogeneous pressure of the reactants is generally sufficient. Where higher pressures are desired, the reaction may be carried out under pressures produced by the addition of gases such as nitrogen or hydrogen.

The process may be carried out in a batch, semicontinuous, or continuous manner. Any apparatus may be used wherein the necessary temperature and liquid phase conditions can be maintained. It is preferred, however, to employ a system from which the water reaction can be removed as it forms. The accompanying drawing illustrates such a preferred system. The manner of carrying out the process in this system will be described using normal butyraldehyde as a typical feed. n-Butyraldehyde is passed in liquid phase at a rate of 0.98 v/v/hr. (volume of feed/volume of catalyst/hour) via line 1 into reactor 2. Reactor 2 is packed with a fixed bed 3 of 0.25-in. (diam.) by 0.25-in. (length) pills

of the molybdenum oxide-magnesium oxide reaction product or the tricomponent catalyst containing zinc oxide. The catalyst bed is maintained at a temperature from 250° F. to 450° F., e.g. 426 F., with electrical resistance heaters 5 or other suitable means. Pressure within the tower is the autogeneous pressure of the reaction mixture, e.g. about 195 psig. The liquid in reactor 2 is maintained at a level sufficient to cover the fixed catalyst bed. Aldolization of the butyraldehyde and dehydration of the condensation product occur in the packed sections of the reactor to produce a mixture of unreacted n-butyraldehyde, water, and 2-ethylhexenal. Under the process conditions, an azeotropic mixture of n-butyraldehyde and water refluxes into the uppermost portion of the column. The azeotrope is removed through line 6 and passed into condenser 7. Light ends in the feed or formed during the reaction are vented from condenser 7 through line 8, while the liquid condensate is passed through line 9 into phase separator 10. The upper layer of condensate which forms in separator 10 is predominantly n-butyraldehyde. This phase is recycled through line 11 into reaction tower 2. The water phase, which contains a minor proportion of N-butyraldehyde dissolved therein, is removed via line 12. The n-butyraldehyde in the water phase may be recovered and recycled if so desired. The aldolization and dehydration product, 2-ethylhexenal, is removed from the catalyst bed through line 13 for further purification and processing.

In another preferred embodiment of the process according to the invention, acetone is passed into a reaction zone maintained at a temperature from 300° F. to 550° F., refluxed in the zone in contact with the catalyst, the water of reaction and acetone in azeotropic combination withdrawn overhead from the zone, the liquid product which comprises mesityl oxide withdrawn.

The following Examples will serve to illustrate the advantages of the present process.

Preparation of catalyst

Equimolar amounts of ammonium molybdate and magnesium oxide, MgO , in powder form were dry-mixed. Sufficient distilled water to produce a thick paste was then added to the mixture. The paste was dried at 400° F. over a period of about 16 hours. The resulting cement-like product was crushed and ground to a fine powder. The powder was passed through a pill press to obtain pills approximately $\frac{1}{4}$ -inch in diameter by $\frac{1}{4}$ -inch in length. The pills were calcined for 16 hours at 1100° F., and then cooled under a dry nitrogen atmosphere prior to their use.

Analysis of the calcined product by X-ray diffraction disclosed that the characteristic lines for molybdenum oxide and magnesium

oxide were absent. Hence, a product of the oxides was formed rather than a mere physical admixture.

EXAMPLE 1

The data obtained in this experiment illustrate the high conversion and high selectivity to 2-ethylhexenal obtained by the condensation of butyraldehyde at two different temperatures and residence times over the catalyst prepared as described above. The n-butyraldehyde was passed downflow in liquid phase

over a fixed bed of about 350 cc. of the piled catalyst at the vapor pressure of the reactant product mixture. Water of reaction was removed overhead as it formed in azeotropic combination with a portion of the n-butyraldehyde feed. External heat was applied with electrical resistance heaters to maintain the catalyst bed at the temperature indicated in Table I. Products were analyzed by gas chromatography. The following results were obtained.

TABLE I

	Run 1	Run 2
Temperature, °F.	350	425
Holding time, hrs.	2.0	1.0
Conversion of n-butyraldehyde, wt. %	75.9	79.2
Selectivity mol % of n-butyraldehyde to 2-ethylhexenal	89.9	86.6

By substituting the aldehydes of Table II for the n-butyraldehyde feed, the following products are produced by the same procedure:

TABLE II

Feed	Product
Acetaldehyde	Crotonaldehyde
Propionaldehyde	2-Methyl pentenal
n-Octyl aldehyde	Hexadecenal
n-Nonyl aldehyde	Octadecenal
n-Lauryl aldehyde	Tetracosenal

EXAMPLE 2

The condensation of acetone and subsequent dehydration to mesityl oxide over the catalyst used in Example 1 was carried out as described in Example 1 except that the water of reaction was not removed from the reaction mixture. The results of Table III were obtained.

TABLE III

Temperature, °F.	400
Holding time, hrs.	2
Acetone conversion, wt. %	11.0
Selectivity to mesityl oxide, mol. %	63.0

In a similar way, methyl ethyl ketone is converted to a mixture of 3-methyl 3-heptene-5-one and 3-methyl 2-heptene-5-one.

EXAMPLE 3

A feed consisting of 2 equivalents acetone per equivalent of isobutyraldehyde was

blended and passed downflow over the catalyst used in Example 1 as described in Example 1. Temperature and holding time are given in Table IV together with a summary of the results:

TABLE IV

Temperature, °F.	475
Holding time, hrs.	1
Acetone conversion wt. %	28.2
Acetone selectivity to MIAK* antecedent, mol %	76.5
Aldehyde conversion, wt. %	63.4
Aldehyde selectivity, to MIAK* antecedent, mol %	72.4
* alpha, beta-unsaturated precursors of methylisoamyl ketone.	

This Example illustrates the applicability of the process to mixed ketone-aldehyde feeds. In a similar manner, a feed comprising methyl ethyl ketone and isobutyraldehyde is converted to a mixture of 3-methyl 3-heptene-5-one, 2-methyl 3-heptene-5-one and 2,4-dimethyl 3-hexene-5-one.

EXAMPLE 4

The use of a catalyst comprising 10 wt. % of the reaction product of molybdenum oxide and magnesium oxide, deposited on a high surface area, alumina, is illustrated in this Example.

A catalyst grade alumina having a surface area from 200 to 250 sq. meters/gram and a pore volume of about 0.64 cc./gram was

calcined at 100° F. for 16 hours. The alumina was then impregnated with sufficient aqueous solution of NH_4MoO_4 to give the desired amount of MoO_3 , and after drying at 250° F., was calcined at 1000° F. for 16 hours. The catalyst support was then similarly impregnated with aqueous $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, dried at 250° F. and calcined at 850° F. for about 16 hours. Substitution of the resultant catalyst for the MoO_3 - MgO reaction product by itself in Example 1 gave the results of Table V:

TABLE V

	Temperature °F.	350
15	Holding time, hrs.	2
	Conversion of n-butyraldehyde, wt. %	75
	Selectivity, mol %, of n-butyraldehyde to 2-ethyl-hexenal	90

Comparison of catalysts.

A catalyst consisting of the reaction product of MoO_3 and MgO , prepared as described in Example 1, was subjected to repeated use under the conditions of Example 1. Examination of the catalyst showed that the pill strength was not adversely affected by repeated use. Furthermore, only negligible attrition, if any, of the pills had occurred.

In contrast, pills of MgO alone, prepared under the same conditions, and pills consisting of a mere admixture of MoO_3 and MgO , disintegrated during a single experiment carried out as in Example 2. Furthermore, the metals content of products obtained in the presence of MgO by itself was prohibitively high as shown by the data in Table VI:

TABLE VI

Feed	ppm Mg in Product	
	MgO Pills	MoO_3 - MgO (reaction product)
n-Butyraldehyde	7500	9.5
Acetone	1500	—

These data further substantiate that the magnesium in the MoO_3 - MgO catalysts of this invention are not present in the same form as in magnesia by itself. The low metals content of the aldolization-dehydration product when the MoO_3 - MgO catalyst is used also illustrates an important advantage of this catalyst. It is apparent that with catalysts containing MgO per se, as with other conventional catalysts such as the soluble metal soaps, a demetalling step is required to reduce the metals content of the products to acceptable levels. This is unnecessary with the MoO_3 - MgO catalysts.

Preparation of catalyst A.

Equimolar amounts of MoO_3 - MgO and ZnO in powder form were dry-mixed. Sufficient distilled water to produce a thick paste was then added to the mixture. The paste was dried at 300° F. The resulting cement-like product was crushed to a fine powder and then compacted in a pill press to obtain pills approximately $\frac{1}{4}$ -in. in diameter by $\frac{1}{4}$ -in. in length. The pills were calcined at 1200° F.

Analysis of the calcined product by X-ray diffraction techniques showed the presence of uncombined zinc oxide; however, the

characteristic patterns for molybdenum oxide and magnesium oxide were absent.

EXAMPLE 5

The following experiments illustrate the high conversions and high selectivities obtained at temperatures from 250° F. to 450° F. when a typical reactant, n-butyraldehyde, is condensed and dehydrated over the catalyst. The n-butyraldehyde was passed downflow in liquid phase into a reactor containing a fixed bed of the pill catalyst. Water of reaction was removed overhead as it formed in azeotropic admixture with a portion of the n-butyraldehyde feed. The butyraldehyde component of the azeotrope was separated from the water in a condensation-separation zone and recycled to the reactor. Product was withdrawn from the bottom of the reactor at such a rate that the liquid reaction mixture covered the fixed catalyst bed. The reaction zone was maintained at the temperature shown in Table VII by means of external electrical resistance heaters around the reactor. Products were analyzed by gas chromatography. The following results were obtained:

TABLE VII

	Run 1	Run 2	Run 3	Run 4
Temperature, °F.	274	350	422	427
Holding time, hr.	3.5	3.4	3	1
Conversion, wt. %	73	82	90	84
Selectivity, *mol. %	83	89	83	88

* To 2-ethylhexenal.

EXAMPLE 6

The catalyst "A" was compared under identical conditions with the oxides and combinations shown in Table VIII. In each case,

the oxides were pilld and calcined as described in Preparation of catalyst A. The experimental procedure of Example 5 was followed, using n-butyraldehyde as the feed.

TABLE VIII

	Catalyst					
	ZnO	MgO	MgO/ZnO	ZnO/MoO ₃	MgO/MoO ₃	A
Temperature, °F.	350	350	350	350	350	350
Holding time, hrs.	2	2	2	2	2	2
Conversion, wt. %	44	80	66	70	76	70
Selectivity,* mol %	66	88	69	83	90	92

* To 2-ethylhexenal

It will be observed that zinc oxide, either alone or in combination with only one of the other oxide ingredients of the present catalyst, gave poorer conversions and selectivities than did the tricomponent catalyst. A further disadvantage of the zinc oxide catalysts, except the tricomponent catalyst, was that the catalyst pills disintegrated during the reaction process. Magnesium oxide alone also suffered in this respect. The only catalyst which approached the tricomponent catalyst in both catalytic activity and ability to withstand the process conditions without crumbling was the molybdenum oxide-magnesium oxide reaction product; however, this catalyst did not give selectivities as high as those obtained with the tricomponent catalysts. The product 2-ethylhexenal produced in the presence of the tricomponent catalyst was water-white.

F. The selectivity to 2-ethylhexenal was 92 mol % with a conversion of 72 wt. %. The product was analyzed and found to contain the following amounts of the catalyst metals.

Metal	Parts Per Million	40
Magnesium	3.1	
Molybdenum	0.15	
Zinc	0.0	
Total	3.25	

Generally, a metals content of below 20 ppm can be tolerated in subsequent processing steps, e.g. hydrogenation. Hence, the 2-ethylhexenal product produced by the present process does not require an additional demetalling step.

EXAMPLE 7

n-Butyraldehyde was condensed and dehydrated in a continuous pilot plant unit containing 350 cc. of the catalyst A. The feed rate was 0.98 v/v/hr. (volumes feed/volumes catalyst/hour) and the temperature was 426°

Preparation of catalyst B

A catalyst comprising zinc oxide, molybdenum oxide, and magnesium oxide in combination with a high surface area support was prepared in the following manner.

A catalyst grade alumina having a surface

area of 234 sq. meters/gram and a pore volume of 0.64 cc./gram was impregnated with 5 wt. % each of the three oxides in the following manner. The alumina catalyst was calcined for 16 hours at 1000° F. The molybdenum oxide was then impregnated on the catalyst in the form of an ammonium molybdate solution which was dried at 250° F. and calcined for 16 hours at 1000° F. The magnesium oxide was then impregnated on the catalyst in the form of a magnesium nitrate solution. This was dried at 250° F. and calcined overnight at 850° F. The zinc oxide was impregnated last as a solution of zinc nitrate and the catalyst dried and calcined in the same way as with the magnesium nitrate. The alumina catalyst containing the three oxides was pillared as described above.

EXAMPLE 8

n-Butyraldehyde was aldolized and dehydrated in a continuous pilot plant unit containing a packed section of the catalyst pellets of Preparation of catalyst B. The carbonyl feed was passed over the pelleted catalyst in liquid phase and water of reaction was removed as it formed by azeotropic distillation with a portion of the n-butyraldehyde. Process conditions and results were as follows:

Temperature, °F.	350
Feed Rate, v/v/hr.	1
Conversion, wt. %	70
Selectivity, mol %	97

The selectivity to 2-ethylhexenal was even superior to the high selectivities (92 mol %) obtained with the unsupported catalyst at the same level of conversion. An additional advantage of the supported catalyst was that feed rates could be approximately doubled over those used with the unsupported catalyst without adversely affecting the weight percent conversion.

EXAMPLE 9

The following experiment illustrates the condensation and dehydration of a typical ketone, acetone, over the catalyst of Preparation A. The process was carried out as described in Example 5. These data were obtained:

Temperature, °F.	450	
Holding time, hrs.	2	50
Conversion, wt. %	13.6	
Selectivity, *mol %	90.3	
*To methyl isobutyl ketone precursors.		

EXAMPLE 10

The following experiment is typical of the co-condensation of a ketone with an aldehyde over the catalyst A. The procedure of Example 5 was followed except that a blend of the two reactants was passed into the reactor. The process conditions and results are given below:

Mole ratio acetone/isobutyraldehyde	3/1	
Temperature, °F.	400	65
Feed rate, v/v/hr.	1	
Acetone conversion, wt. %	28	
i-Butyraldehyde conversion, wt. %	37	
Acetone selectivity to MIAK* antecedent, mol %	80	70
i-Butyraldehyde selectivity to MIAK* antecedent, mol %	69	
*Alpha, beta-unsaturated precursors of methylisobutyl ketone		

EXAMPLE 11

Acetone and isobutyraldehyde were co-condensed in a continuous pilot unit over the supported catalyst B. Process conditions and results are given below.

Mole ratio acetone/isobutyraldehyde	3/1	3/1
Temperature, °F.	350	426
Feed rate, v/v/hr.	1	1
Acetone conversion, wt. %	14	23
i-Butyraldehyde conversion, wt. %	46	88
Acetone selectivity to MIAK antecedent, mol %	91	85
i-Butyraldehyde selectivity to MIAK antecedent, mol %	85	80

EXAMPLE 12

The data given in the following table further illustrate the variety of carbonyl feeds which can be condensed and dehydrated over the tricomponent catalyst of the present in-

vention to provide alpha, beta-carbonyl compounds of increased molecular weight. In each instance, the catalyst was that described in Preparation of Catalyst B.

Feed	Temp. °F.	Contact Time, Hrs.	Conversion, wt. %	Selectivity,* Mol %
i-Octanal	450	1	58	90
i-Decanal	450	2	40	90
10 Methyl ethyl ketone	450	2	11	90
" " "	1/1 molar ratio 450	1	60	80
i-Butyraldehyde				

* To alpha, beta-unsaturated carbonyl products.

The alpha, beta-unsaturated aldehydes and ketones produced by the process of the present invention can be selectively hydrogenated catalytically with conventional catalysts and under conventional conditions, for example, with Raney nickel supported on kieselguhr at from 200° to 250° F. and 200 psig hydrogen partial pressure, to produce the corresponding saturated aldehydes and ketones. Alternatively, the unsaturated reaction products may be completely hydrogenated under more severe conditions to the corresponding alcohols, for example, at from 250° to 400° F. and 3000 psig hydrogen partial pressure.

WHAT WE CLAIM IS:—

1. A process for producing alpha, beta-unsaturated carbonyl compound which comprises contacting a liquid feed containing a monofunctional, aliphatic C₂ to C₁₀ aldehyde and/or ketone having at least two alpha hydrogen atoms at from 50° to 600° F. with a catalyst produced by reacting together at elevated temperature the trioxide of molybdenum and an oxide of magnesium or other compounds of these metals which produce these oxides at the elevated temperature.

2. A process as claimed in claim 1, wherein the liquid feed comprises in addition an inert solvent.

3. A modification of the process as claimed in Claims 1 or 2, wherein the catalyst contains also zinc oxide.

4. A process as claimed in Claims 1 to 3, wherein the catalyst includes a high surface area catalyst support.

5. A process as claimed in Claims 1 to 4, wherein the catalyst is obtained by calcining a mixture of the oxides at a temperature from 300° to 1500° F.

6. A process as claimed in Claims 1 to 5, wherein at least one of the oxides is formed *in situ*.

7. A modification of the process as claimed in Claims 1 to 6, wherein the feed comprises in addition a monofunctional, aliphatic aldehyde or ketone.

8. A process as claimed in any preceding claim, wherein the oxides are used in equimolar proportion.

9. A process as claimed in any preceding claim, wherein the carbonyl compound in the liquid feed is a C₂ to C₁₀ aliphatic aldehyde having at least two alpha hydrogen atoms.

10. A process as claimed in any of Claims 1 to 8, wherein the carbonyl compound in the liquid feed is a C₂ to C₁₀ aliphatic ketone having at least two alpha hydrogen atoms.

11. A process as claimed in any preceding claim, which comprises passing n-butyraldehyde into a reaction zone maintained at a temperature of from 250° F. to 450° F., refluxing the n-butyraldehyde in contact with the catalyst, withdrawing water of reaction and n-butyraldehyde in azeotropic combination overhead from this zone, and recovering a liquid product comprising 2-ethylhexenal.

12. A process as claimed in Claim 11, wherein the water-n-butyraldehyde azeotrope is condensed, the condensate separated into a predominantly water phase and a predominantly n-butyraldehyde phase, and the latter phase is recycled to the reaction zone.

13. A process as claimed in Claim 10, which comprises passing acetone into a reaction zone maintained at a temperature from 300° F. to 550° F., refluxing the acetone in the zone in contact with the catalyst, withdrawing water of reaction and acetone in azeo-

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tropic combination overhead from the zone, and recovering a liquid product comprising mesityl oxide.

- 5 14. A process as claimed in Claim 1, substantially as described with reference to the Examples.

15. A process as claimed in Claim 3, substantially as described with reference to the Examples.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54, High Holborn,
London, W.C.1,
Agents for the Applicants.

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1,010,695 COMPLETE SPECIFICATION

1 SHEET

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